Supplementary Information for

3D Fluorescent Mapping of Invisible Molecular Damage after Cavitation in Hydrogen Exposed Elastomers

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Legends for Movies S1 to S4

Other supplementary materials for this manuscript include the following:

Movies S1 to S4

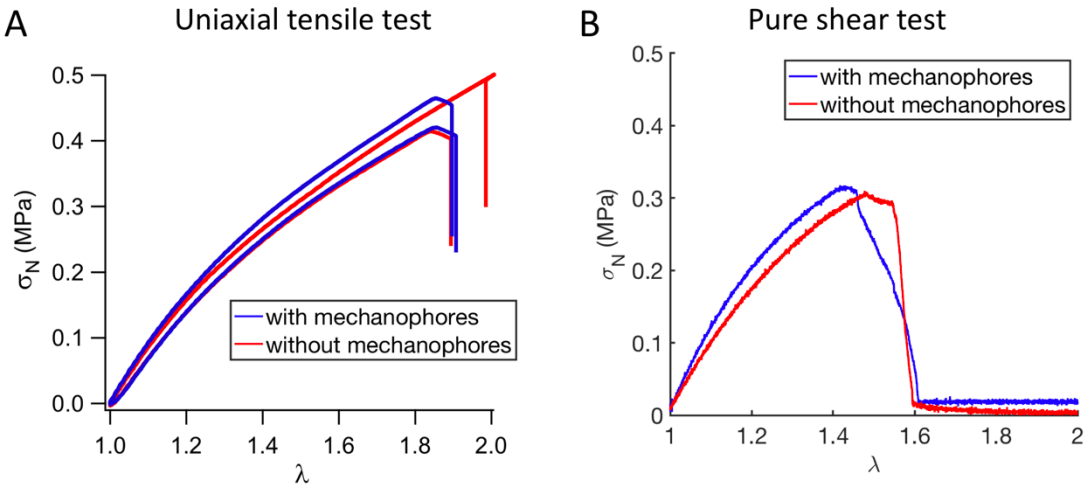

Fig. S1. Comparison of the mechanical properties of the ethyl-acrylate polymer network with or without mechanophores. No significant differences in elastic and fracture properties can be noticed both under (A) uniaxial tensile tests; and (B) pure shear tests.

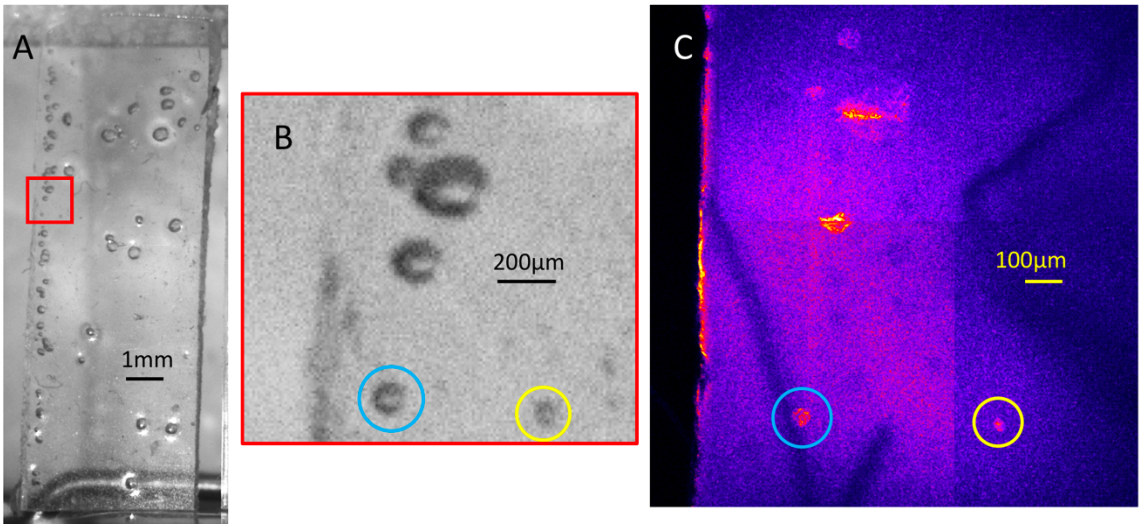

Fig. S2. (A) Optical snapshot of second ethyl acrylate specimen (see Movie S2) at maximum cavity expansion during decompression at 10MPa/min after 10h of saturation at a pressure of 5 *MPa* of hydrogen. (B) Zoom on the red square region of (A) where six cavities can be seen, among which the smaller one (yellow circle) is hardly visible by our camera. (C) is the confocal (top view) zoom of the region corresponding to the red square in (A) where a localized fluorescent damage region can be found for each of the six cavities identified in (B). The damaged region of the yellow cavity has a disc shape with a diameter size as small as 30 *µm*.

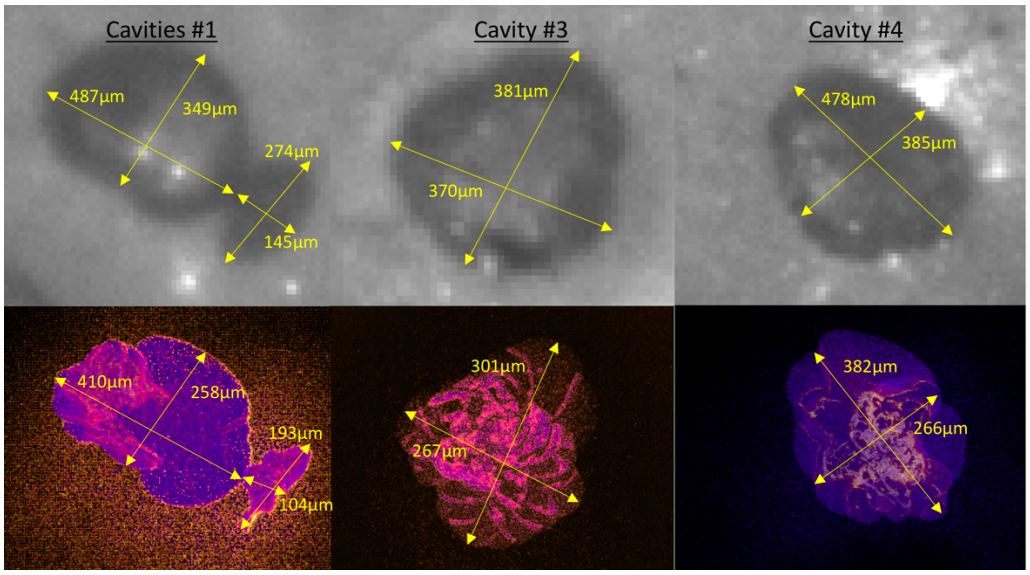

Fig. S3. Size comparison between maximum (inflated) cavity through optical visualization (top) and associated damage region, in the deflated state, visualized by fluorescent microscopy. The identified cavities correspond to the number-identification on FIG2A and are fortuitously well-aligned with the specimen xy-plane.

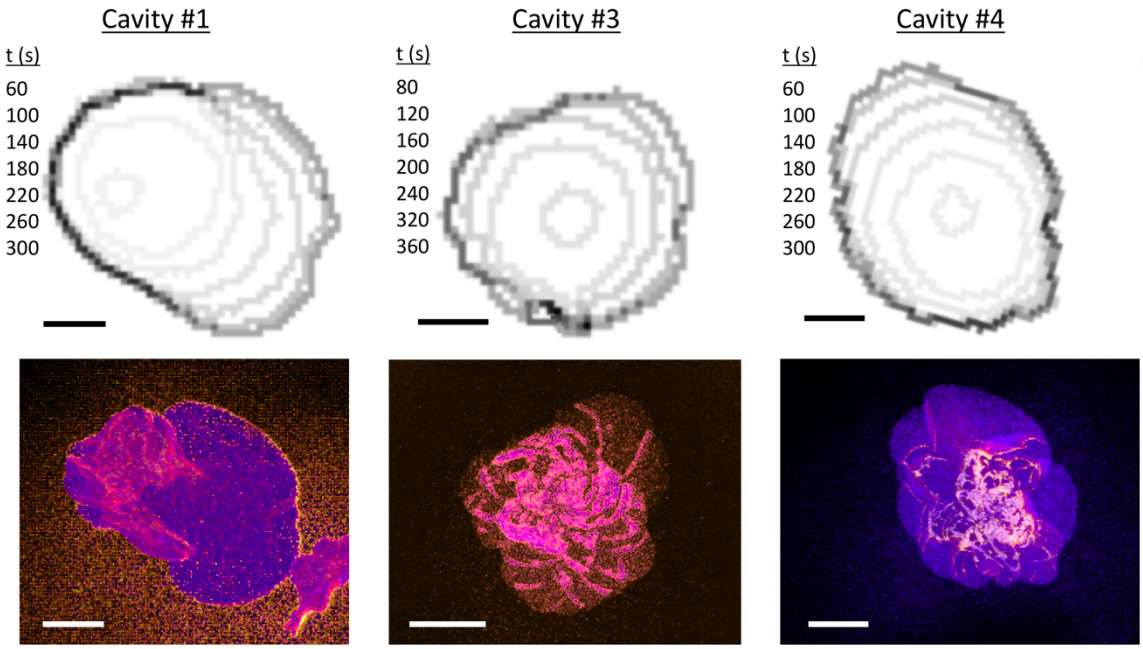

Fig. S4. (top) Cavity contour evolution at constant different (constant) time step obtained from optical visualization during decompression (NB: 2D projection limitation thus apply). (bottom) Confocal (artistic) top view of corresponding cavities in order to highlight the difference of fluorescence intensity (and overall contour) between nucleation site and the rest of the flower-like pattern. The 3 visualized cavities correspond to the number-identified on FIG2A, white and black scale bars correspond to 100 *μm*.

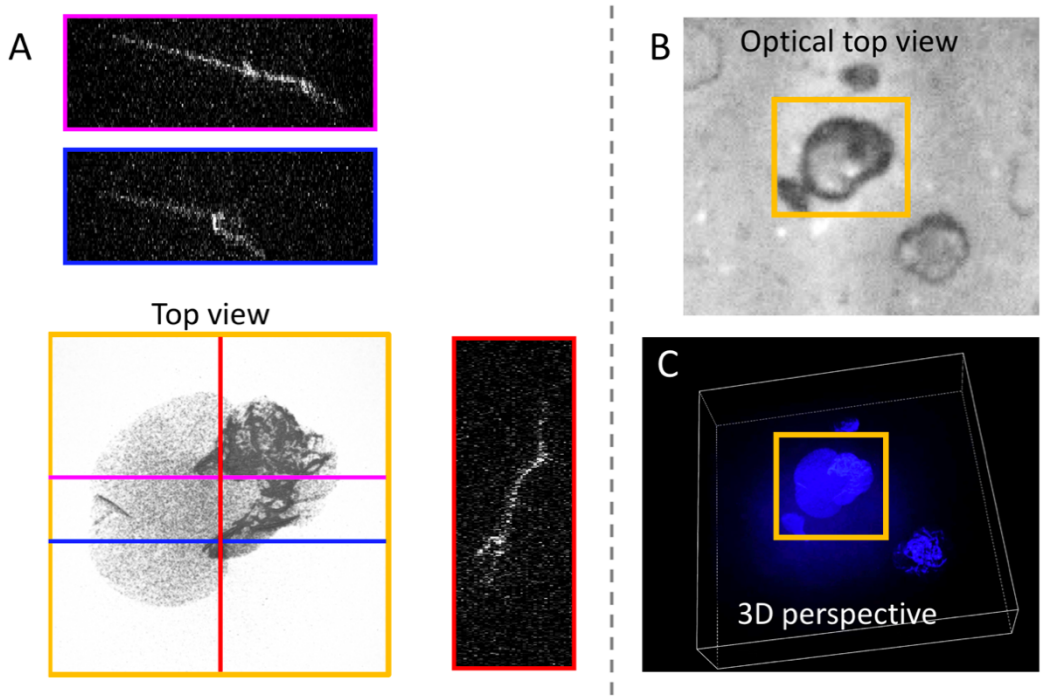

Fig. S5. (A) Confocal fluorescent microscopy of the biggest central cavity highlighted with a yellow square in (B) and (C), with corresponding cross-sectional images highlighting local crack bifurcation and tilt of cavity damage region. (B) & (C) are respectively the optical (in the maximum inflated state) and confocal (in the deflated state) view of overall Zone 2 identified in FIG 2.

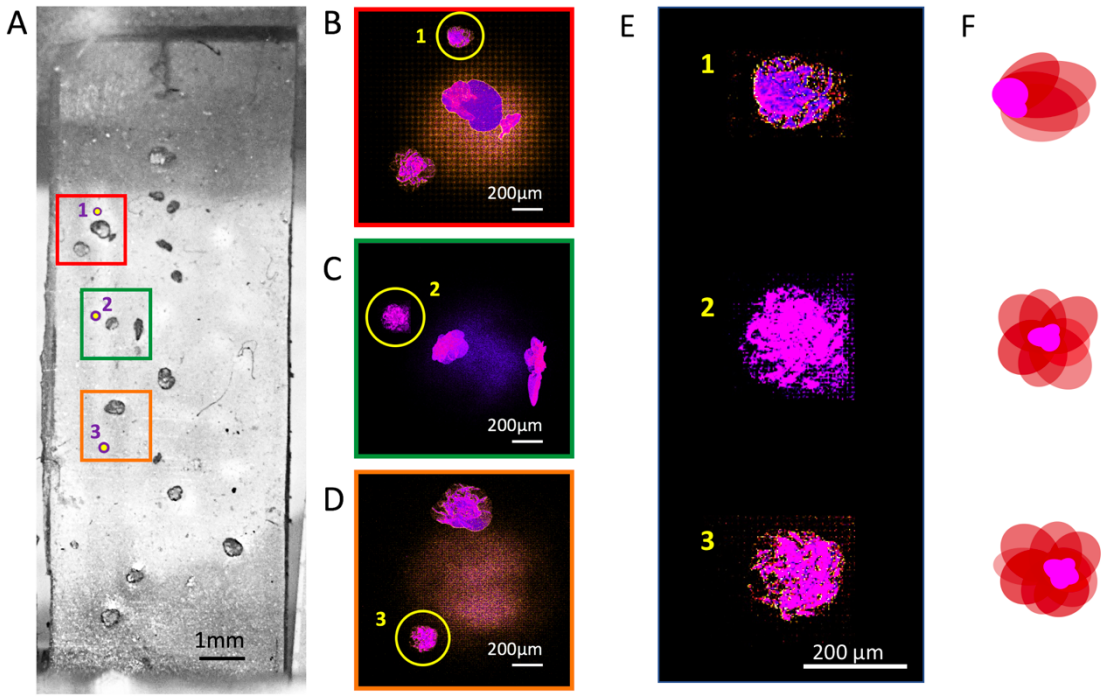

Fig. S6. (A) Optical snapshot of our ethyl acrylate elastomer specimen at maximum cavity expansion during decompression, highlighting three colored regions each one with a cavity exhibiting only a self-similar spherical growth (violet circle with yellow dot). (B), (C) and (D) are respectively the confocal (top view) zoom of the corresponding fluorescent damaged regions. The three seemingly spherical cavities are numbered and highlighted with yellow circles with corresponding magnified zoom shown in (E). The fluorescent signal provides a better optical resolution and shows that the damage associated to each of these cavities also corresponds to the superposition of penny-shape cracks forming a flower like pattern (F), hence confirming the same damage growth mechanism than for larger anisotropic cavities. (note that the centered orange or purple halo in (B), (C) and (D) is an optical artifact coming from the fluorescence of the specimen surface.)

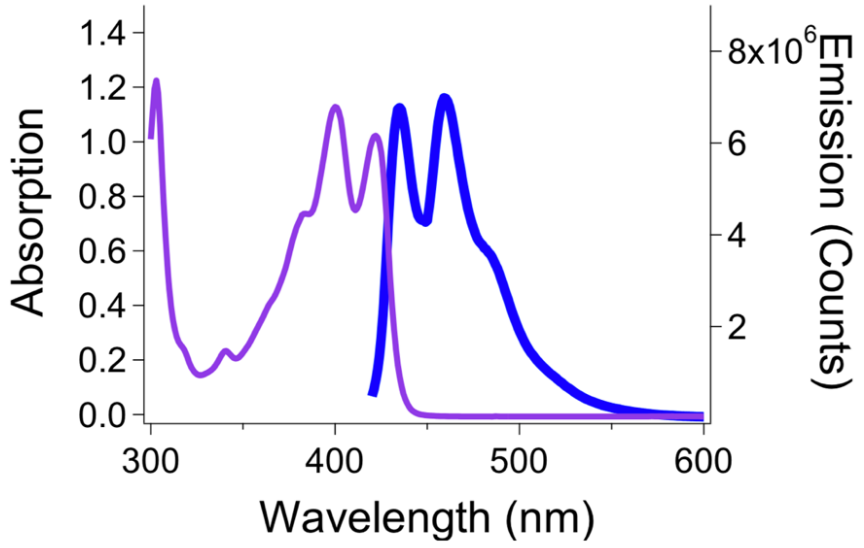

Fig. S7. Absorption and emission peak of π-extended anthracene moieties, data taken from [1]. Photoluminescence and excitation spectra were obtained from an Edinburgh Instrument spectrometer. The absorption spectrum was recorded between 320 *nm* and 450 *nm* for an emission at 460 *nm*. The emission spectrum was recorded between 420 *nm* and 600 *nm*, for an excitation at 405 *nm.* The reference molecule was diluted in ethyl-acetate at $6x10^{-5}$ $mol.L^{-1}$.

Movie S1 (separate file). Video made of the snapshots (every 20 s until 400s then every 100s until 1100s) of the different stages during and after a decompression at 10MPa/min of an ethyl-acrylate elastomer saturated at a pressure of 5 MPa of hydrogen for 10 h. The specimen depicted is the same as the one studied through the entire article and totally or partially shown in FIG2, 3 and 4.

Movie S2 (separate file). Video made of the 3D mapping with a confocal microscope of the fluorescent damage zones corresponding to the cavities pictured in the red frame (n°1) of Figure 2. The video starts by a progressive z-scan of the region of interest followed by 3D rotation.

Movie S3 (separate file). Video made of the snapshots (at various intervals from 18s to 1800s) of the different stages during and after a decompression at 10MPa/min of a second ethyl-acrylate elastomer specimen saturated at a pressure of 5 MPa of hydrogen for 10 h.

Movie S4 (separate file). Video made of the snapshots (accelerated 40x) of the different stages during and after a decompression at 5MPa/min of 3 samples of ethyl-acrylate elastomer (the right one with mechanophores and the two left ones without) saturated at a pressure of 5 MPa of hydrogen for 10 h, confirming no significant difference of cavitation resistance (especially no embrittlement) is observed.

SI References

1. Slootman, J., *Quantitative detection of damage in soft materials using mechano-fluorescence*, in *ESPCI Paris*. 2019, PSL.